The Molecular Rearrangement of Symmetrical Bis-Triphenylmethylhydrazine

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE
SCHOOL OF SCIENCE IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

RALPH LYMAN BROWN

The Molecular Rearrangement of Symmetrical Bis-Triphenylmethylhydrazine

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE
SCHOOL OF SCIENCE IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

RALPH LYMAN BROWN

The University of Chicago

Molecular Rearrangement of Symmetrical
Bis-Bromomethyl Ketone

A DISSERTATION

THE MOLECULAR REARRANGEMENT OF SYMMETRICAL BIS-TRIPHENYLMETHYLHYDRAZINE[1]

Organic hydrazine derivatives resemble derivatives of hydroxyl-amine in all fundamental characteristics, except that, with a single exception, they have not been found to undergo molecular rearrangements of the same type as the Beckmann rearrangement of oximes or the Lossen rearrangement of hydroxamic acids. Stieglitz and Senior,[2] who called attention to this difference, made a series of attempts to effect such rearrangements of hydrazine compounds, but all their efforts were unsuccessful except when they used *sym.-bis*-triphenyl-methylhydrazine, $(C_6H_5)_3C.NH.NH.C(C_6H_5)_3$. When they heated this compound to 250° to 300° with anhydrous zinc chloride and hydrolyzed the reaction product, aniline was obtained, which proved conclusively that one of the phenyl groups of the triphenylmethyl radicals migrates under these conditions from carbon to nitrogen, which is the typical shift of the Beckmann-Lossen rearrangements, and of the analogous rearrangements in the triphenylmethane series discovered by the one of us and his collaborators.[3] The only other product identified in the preliminary investigation was triphenylmethane, a product of a parallel thermal decomposition of the hydrazine.

The present paper reports the results of a continuation of the investigation, which was carried out to throw light on the mechanism of the rearrangement. Unexpected results obtained toward the end of the investigation have made it impossible, at the present moment, to give a complete theory of the reaction, but as the one of us (Brown) was called to service in the U. S. Army, we wish to present now the lines of thought
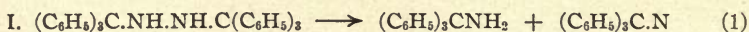
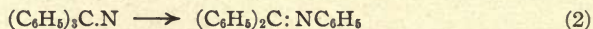[2] *Proc. Nat. Acad. Sci.*, **1**, 207 (1915); and *J. Am. Chem. Soc.*, **38**, 2727 (1916).

[3] See the literature references in *J. Am. Chem. Soc.*, **36**, 272 (1914) and **38**, 2051 (1916).

followed as working hypotheses and the relation of the results obtained, to these views.

By analogy to other rearrangements of this type, two possible courses of the rearrangement reaction are suggested at the outset.[4] In the first place, according to the theory of the one of us,[5] we might have as the primary action offering least resistance a decomposition of the hydrazine compound into triphenyl-methylamine and triphenyl-methylimide, a univalent nitrogen compound which would undergo the rearrangement proper
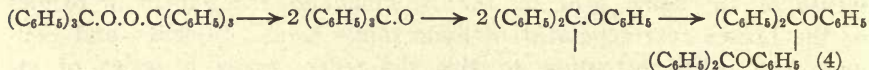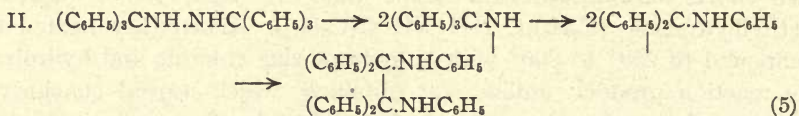
$$\text{I.} \quad (C_6H_5)_3C.NH.NH.C(C_6H_5)_3 \longrightarrow (C_6H_5)_3CNH_2 + (C_6H_5)_3C.N \qquad (1)$$

and

$$(C_6H_5)_3C.N \longrightarrow (C_6H_5)_2C:NC_6H_5 \qquad (2)$$

By hydrolysis of the phenylimido-benzophenone thus formed, aniline and benzophenone would be produced.

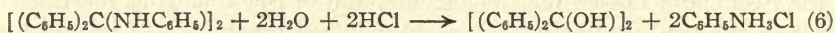$$(C_6H_5)_2C:NC_6H_5 + HOH + HCl \longrightarrow (C_6H_5)_2CO + C_6H_5NH_3Cl \qquad (3)$$

The alternative course of the reaction would be a rearrangement akin to the rearrangement of triphenylmethyl-peroxide, as investigated by Wieland.[6]

$$(C_6H_5)_3C.O.O.C(C_6H_5)_3 \longrightarrow 2\,(C_6H_5)_3C.O \longrightarrow 2\,(C_6H_5)_2C.OC_6H_5 \longrightarrow \underset{(C_6H_5)_2COC_6H_5}{(C_6H_5)_2COC_6H_5} \qquad (4)$$

Bis-triphenylmethylhydrazine might rearrange in an analogous way as follows.

$$\text{II.} \quad (C_6H_5)_3CNH.NHC(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C.NH \longrightarrow 2(C_6H_5)_2C.NHC_6H_5$$
$$\longrightarrow \underset{(C_6H_5)_2C.NHC_6H_5}{(C_6H_5)_2C.NHC_6H_5} \qquad (5)$$

Hydrolysis of the resulting product, if it occurred at all, would lead to the formation of aniline and benzopinacone.

$$[(C_6H_5)_2C(NHC_6H_5)]_2 + 2H_2O + 2HCl \longrightarrow [(C_6H_5)_2C(OH)]_2 + 2C_6H_5NH_3Cl \qquad (6)$$
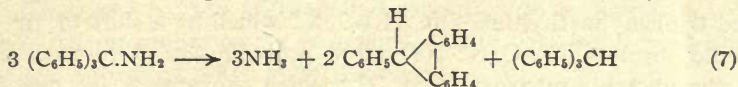
In the experimental part of this report, it will be shown that, besides aniline, which was again identified after hydrolysis of the reaction product, *benzophenone* was isolated and identified, a result which decidedly favors the mechanism of the reaction expressed under I. The third product of the reaction required by Scheme I is triphenyl-methylamine. This was not found, but it was suspected that any triphenyl-methylamine formed would be decomposed by the zinc chloride at the temperature of the reaction. For that reason, the effect of zinc chloride on the amine was studied. As anticipated, when triphenyl-methylamine reacts with zinc

---

[4] The interpretation from the point of view of the electron conception of valence will be given further on in this paper.

[5] See the literature references given by Stieglitz and Leech, *J. Am. Chem. Soc.*, **36**, 272 (1914) and by Stieglitz and Stagner, *ibid.*, **38**, 2051 (1916).

[6] Wieland, *Ber.*, **44**, 2550 (1911).

chloride, the chief products of decomposition are ammonia, phenyl-di-phenylenemethane and triphenylmethane.   For instance, we may have

$$3 \ (C_6H_5)_3C.NH_2 \longrightarrow 3NH_3 + 2 \ C_6H_5C \overset{H}{\underset{C_6H_4}{\overset{C_6H_4}{\Big\langle}}} + (C_6H_5)_3CH \qquad (7)$$
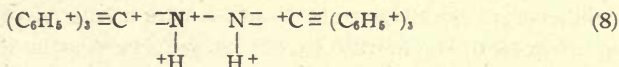
This action is analogous to the decomposition of triphenylmethyl chloride and bromide by heat and of the corresponding carbinol by phosphorus pentoxide.

Returning now to the examination of the products of the rearrangement of *bis*-triphenylmethylhydrazine, we have found without difficulty that ammonia and phenyl-diphenylenemethane, besides triphenylmethane, are indeed formed in the reaction.   Furthermore, quantitative determinations, which will be discussed at greater length presently, showed that the amount of ammonia, *i. e.*, triphenyl-methylamine as the primary product formed is of the order demanded by the equations given under I.

Thus far, all the experimental evidence, therefore, favors the conception that the rearrangement of *bis*-triphenylmethylhydrazine by zinc chloride follows the course through a univalent nitrogen derivative which seems to be the same as that commonly followed as the path of least resistance[7] in the rearrangement of oximes, hydroxamic acids, chloro- and bromo-amides of the acids, acyl azides, triarylmethyl-azides, -hydroxylamines and -chloro-amines, as grouped together by the theory of the one of us. Exhaustive examination of the reaction products brought to light further facts, some of which have raised novel and interesting questions.   Before these are presented, it seems wisest to complete the discussion of the rearrangement proper by referring as briefly as possible to the interpretation of the rearrangement from the point of view of the electron conception of valence.[8]   The discussion from this fundamental point of view will greatly facilitate the consideration of the further experimental results to be presented below.

For *bis*-triphenylmethylhydrazine we have the electronic structure[9]

$$(C_6H_5{}^+)_3 \equiv C^+ \ \overline{}N^{+-} \ N\overline{} \ {}^+C \equiv (C_6H_5{}^+)_3 \qquad (8)$$
$$\underset{+H}{|} \qquad \underset{H+}{|}$$

The atom with an unstable positive charge, as postulated by the one of us as occurring in all of the rearranging compounds of this character, in the present instance is one of the two otherwise apparently symmetrical nitrogen atoms: for the sake of convenience we have designated the unstable nitrogen atom with the positive charge in question by putting it in heavy type as $\mathbf{N}^+$.   In the formation of a rearranging univalent nitrogen derivative, either of the following courses may be followed:

[7] Stieglitz, *Proc. Nat. Acad. Sci.*, Ref. 2.   Stieglitz and Stagner, Ref. 5.

[8] Stieglitz and Leech, Ref. 5.   Jones, *Am. Chem. J.*, **50**, 440 (1913).

[9] Only those charges are indicated which bear on the discussion.

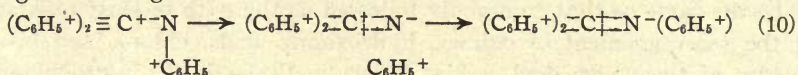(1) the true ammonia nitrogen atom $^-$N$^-_-$ deprives the nitrogen atom $_-$N$^+$ of its hydrogen atom, forming triphenylmethyl-amine $(C_6H_5)_3C.NH_2$ and triphenylmethyl-imide $(C_6H_5)_3C.N^{\pm}$ which by a shift of the electron would form $(C_6H_5)_3C.N$; (2) more probably *the disturbance originates* in the unstable nitrogen atom $_-$N$^+$ which captures 2 electrons from the neighboring nitrogen atom. With the accompanying migration of the hydrogen atom lost by $^-$N$^-_-$ as a result of the loss of its electrons, this gives

$$(C_6H_5{}^+)_3 \equiv C^{+-}N^-_-(^+H)_2 \text{ and } N^{-+}C \equiv (C_6H_5{}^+)_3 \tag{9}$$
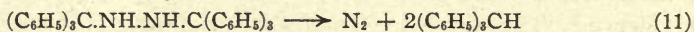
As a basis of choice between these two possible courses we have no experimental information except that *the second course* would be exactly analogous to the changes occurring in the closely related rearrangements of halogen amides, oximes, etc. A final decision between these two paths would be, we believe, of great importance, since therein most likely will be found the key to the interesting fact that this *symmetrical* hydrazine rearranges, whereas all the unsymmetrical hydrazines examined by Senior and the one of us are not rearranged.[10]

In either case, we have then, further, the normal course for univalent nitrogen rearrangements[11]

$$(C_6H_5{}^+)_2 \equiv C^{+-}N \longrightarrow (C_6H_5{}^+)_2{}_-C{}^+_-{}_-N^- \longrightarrow (C_6H_5{}^+)_2{}_-C{}^+_-{}_-N^-(C_6H_5{}^+) \tag{10}$$
$$\begin{array}{ccc} | & & \\ ^+C_6H_5 & & C_6H_5{}^+ \end{array}$$

Two electrons migrate from the methyl carbon from the valence indicated by the sign in heavy type to the univalent nitrogen atom, the released positive phenyl group migrating to the free negative charge on the nitrogen.

Returning now to the further observations made in the course of the experimental work, we would mention first that the formation of triphenylmethane and nitrogen

$$(C_6H_5)_3C.NH.NH.C(C_6H_5)_3 \longrightarrow N_2 + 2(C_6H_5)_3CH \tag{11}$$

observed by Senior and the one of us, was conclusively shown to be a thermal decomposition. The electronic interpretation is given in the preliminary paper[12] and shows that the decomposition is the result of an intramolecular oxidation-reduction in which the electrons migrate *from* the nitrogen to the methyl carbon atom, whereas the molecular rearrangement just discussed, which is also the result of an intramolecular oxidation-reduction reaction, involves a migration of electrons from the methyl carbon *to* the nitrogen, this course being the direct reverse of that followed in the thermal decomposition. The decomposition by heat and the rearrangement are therefore the results of two parallel and competing oxi-

---

[10] The interpretation is given by Stieglitz and Senior, Ref. 2 [*J. Am. Chem. Soc.*] p. 2729. Since this was written, Messrs. E. C. Gilbert and J. F Smith in this Laboratory have effected the rearrangement of a number of hydrazine derivatives, including benzophenone-hydrazone. (May, 1922).—J. S.

[11] See Stieglitz and Leech, and Stieglitz and Stagner, Ref. 5.

[12] Ref. 2 (*J. Am. Chem. Soc.*, p. 2731).

dation-reduction reactions of an intramolecular character. One of the main experimental difficulties encountered was the problem of reducing the loss of material by the thermal decomposition to a minimum. At best a yield corresponding to the rearrangement of somewhat more than a third of the substance was finally obtained.
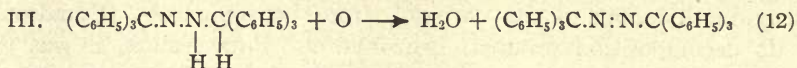
The next observations made were not anticipated and have raised new questions of interest. Among the reaction products *phenol* was obtained in appreciable quantities. It was at first thought that its presence might be due to some decomposition of the aniline group in phenylimido-benzophenone, the zinc chloride, when it is present in large excess, possibly reversing the well-known change of phenol into aniline by zinc-ammonium chloride.[13] Experiments made with phenylimido-benzophenone and zinc chloride proved that this is not the source of the phenol. Nothing was found in the literature indicating the formation of phenol from tri-phenyl-methylamine or its carbinol, from benzopinacone (Equation 6) or its decomposition product, benzohydrol. Furthermore, it was then found that when *bis*-triphenylmethylhydrazine is heated with zinc chloride *in the absence of air*, for instance in an atmosphere of carbon dioxide, no phenol is formed, but the formation of diphenyl is strongly suggested by its odor. The carrying out of the action in the presence of carbon dioxide in place of air led to the further unexpected observation that under these conditions there is *no rearrangement* to an aniline derivative; at most, small quantities of aniline were obtained in the working up of the products, which might be due to the presence of occluded air in the reagents used. These results open up a series of interesting questions, which can only be suggested here as the basis on which further investigation is being planned.

It is evident, in the first place, that the production of phenol is due to the oxidation of a phenyl radical at some stage of the action at the expense ultimately of the oxygen of the air. Two interesting possibilities suggest themselves. Phenol may be formed by the capture of oxygen by some of the phenyl radicals before they have reached their destination, the nitrogen atoms (see the middle phase of the action represented in Equation 10). Whether the phenyl radicals, originally positive, first capture some of the migrating electrons which lead to the rearrangement, and escape because they have become electrically neutral is a matter of fascinating speculation which can only be suggested here. In support of this conception we have the fact that the formation of *diphenyl* is indicated, as yet only by its odor, especially when oxygen is excluded. As far as we can discover, the formation of compounds of the type of phenol and diphenyl has never been observed before in the numberless rearrangements in which an aryl or an alkyl group migrates from carbon to nitrogen,
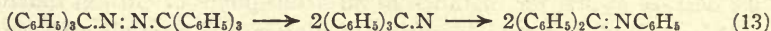
[13] Merz and Weith, *Ber.*, **13**, 1299 (1880).

but none of these has been carried out, as far as we can find, at so high a temperature as 300°.
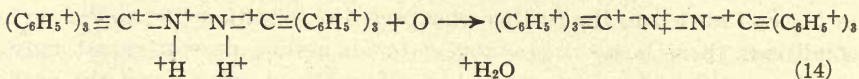
In the second place, Wieland[14] found that when azo-triphenylmethane is formed by oxidation of *bis*-triphenylmethylhydrazine, it decomposes at once, even at 0°, into triphenylmethyl: this compound is oxidized by air to its peroxide, which in turn is rearranged by heat into the diphenyl ether of benzopinacone (Equation 4). This phenol derivative may be the source of the phenol obtained in our reaction. Wieland found, however, that the hydrazine is not oxidized to the azo compound by air, but requires more powerful oxidizing agents. It is possible, nevertheless, that at 300° a temperature never attained in Wieland's experiments, oxidation by air does occur. Furthermore, part of the azo compound might undergo the rearrangement leading to the formation of phenylimido-benzophenone, as follows.
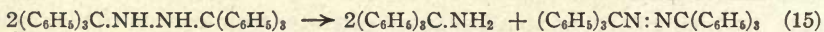
III. $\quad (C_6H_5)_3C.N.N.C(C_6H_5)_3 + O \longrightarrow H_2O + (C_6H_5)_3C.N:N.C(C_6H_5)_3 \quad (12)$
$\qquad\qquad\ \overset{|}{H}\ \overset{|}{H}$

and

$\qquad (C_6H_5)_3C.N:N.C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C.N \longrightarrow 2(C_6H_5)_2C:NC_6H_5 \quad (13)$

Electronically, we would have

$(C_6H_5{}^+)_3 \equiv C^+ \equiv N^+ {}^-N \equiv {}^+C \equiv (C_6H_5{}^+)_3 + O \longrightarrow (C_6H_5{}^+)_3 \equiv C^+ {}^-N \ddagger \equiv N^{-+}C \equiv (C_6H_5{}^+)_3$
$\qquad\quad \overset{|}{{}^+H}\ \ \overset{|}{H^+} \qquad\qquad\qquad\qquad\qquad {}^+H_2O \qquad\qquad\qquad\qquad (14)$

Two electrons leave the nitrogen at the point indicated by the negative sign in heavy type, with the formation of water and azo-triphenylmethane. The dissociation of the latter into two molecules of triphenyl-methylimide $(C_6H_5)_3C.N$, needs no further explanation and the rearrangement of the imide would follow the course indicated in Equation 2 above.

No rearrangement of this kind was ever observed by Wieland in his attempts to prepare azo-triphenylmethane, and while the reaction which he did observe (decomposition into nitrogen and triphenylmethyl) was carried out in the cold (usually at 0°), a higher temperature would presumably simply accelerate this decomposition. Nevertheless, some of Wieland's work will be repeated as soon as circumstances permit, and efforts especially made to isolate azo-triphenylmethane in order that it may be subjected to sudden heating to 300°.

This interpretation still fails to account for the formation of the decomposition products of triphenyl-methylamine. To account for these we would have to assume that at 300° still another decomposition of the hydrazine occurs, never observed in its study, but analogous to the well-known decomposition of hydrazobenzene into aniline and azobenzene.

$2(C_6H_5)_3C.NH.NH.C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C.NH_2 + (C_6H_5)_3CN:NC(C_6H_5)_3 \quad (15)$

[14] Wieland, *Ber.*, **42**, 3020 (1909).

In that event, the azo compound must be formed and rearrangement should occur even in the absence of air, which does not seem to be the case.

If we assume, therefore, for the present simply as a working hypothesis that the course of the action is that given in Scheme I and that the formation of phenol is actually due to the oxidation of phenyl groups escaping rearrangement, then for every molecule of triphenyl-methylamine formed there should be produced either a molecule of phenylimido-benzophenone (Equations 1 and 2) or a molecule of phenol. The quantity of triphenyl-methylamine produced is found by the quantitative determination of its decomposition product, ammonia, and the quantity of phenylimido-benzophenone produced is found from a volumetric assay of the aniline formed by its hydrolysis. In addition, the quantity of phenol obtained was also determined volumetrically. Now, according to what has been developed above, the interpretation of the rearrangement outlined under I demands that the sum of the aniline and the phenol formed should be roughly of the order[15] of the amount of ammonia (triphenyl-methylamine) obtained. This result is well borne out by the experimental values as collected in Table II.

Experimental Part[16]

I. **Preparation of** *sym.-bis*-**Triphenylmethylhydrazine,** $(C_6H_5)_3CNH.-NHC(C_6H_5)_3$.—For the purpose of obtaining better yields, the compound was prepared by the treatment of triphenylmethyl bromide rather than of the corresponding chloride,[17] with hydrazine hydrate.

The triphenylmethyl bromide was prepared according to the method of Allen and Kölliker[18] and recrystallized from benzene. To the hydrazine hydrate (8 g.), covered with absolute ether (100 cc.), the triphenylmethyl bromide (27.4 g., 95% pure) was added in small portions throughout the course of about an hour, the mixture being constantly shaken. The reaction began immediately on the introduction of the bromide and proceeded at ordinary temperatures with evolution of heat and continuous precipitation of the *sym.-bis*-triphenylmethylhydrazine and hydrazine hydrobromide. The action was practically complete a short time after the last portion of triphenylmethyl bromide was added, but the reaction mixture was allowed to stand for a day to insure completion. The precipitate was collected on a filter and washed, in turn, with ether,

---

[15] Every molecule of triphenyl-methylamine formed gives a corresponding molecule of ammonia, our experiments having shown that the ammonia formation is practically quantitative when triphenyl-methylamine is heated with zinc chloride. But some of the phenyl groups may well escape combination with oxygen or with nitrogen. Thus, the formation of diphenyl was strongly indicated in the last experiment undertaken. The sum of the aniline and phenol formed should, therefore, be rather somewhat smaller than greater, than the amount of ammonia produced.

[16] I wish to use this opportunity to express my appreciation of the skilful and painstaking manner in which my young collaborator, Mr. Brown, has handled the rather complex experimental material which this problem has presented. All the experimental work was carried out by Mr. Brown.—J. S.

[17] Ref. 14, pp. 3021, 3025. Ref. 19, p. 2727.

[18] Allen and Kölliker, *Ann.*, **227**, 110 (1885).

alcohol, water, very dilute sodium hydroxide solution, water, alcohol and ether. The yield was 12.9 g. of crude material melting at 213°. Further purification by the method of Wieland gave 11.2 g. of the compound melting at 216°. A second recrystallization raised the melting point to 219–220°. Since decomposition takes place at the melting point, the melting-point tube containing the material was introduced into the temperature bath when it was 5° below the melting point of the compound.

II. A Study of the Decomposition of *sym.-bis*-Triphenylmethylhydrazine at its Melting Point

The fact that the only evidences of a rearrangement had been obtained when the compound had been heated with zinc chloride at a temperature higher than that of its melting point, made a study of the melting-point decomposition imperative. At its melting point in air, *bis*-triphenylmethylhydrazine showed a marked evolution of gas and gave as a residue a dirty-white solid melting without purification at 85°. This residual solid mixed with triphenylmethane[19] melting at 92°, gave a melting point of 87°–90°. A sample of 1.5 g. of the *bis*-triphenylmethylhydrazine was then heated at 220–230° in an atmosphere of dry carbon dioxide until all evolution of gas ceased and the gas had been swept into a nitrometer filled with 50% potassium hydroxide solution. The residual material, while molten, was an amber colored liquid and in the solid state was a yellowish white substance.

The gas was examined first. It showed no loss of volume when passed through a palladium black tube, such as is used for determinations of hydrogen by absorption, nor when passed into potassium hydroxide, ammoniacal cuprous chloride and phosphorus pipets. This eliminates the possibility of hydrogen, unabsorbed carbon dioxide, carbon monoxide and oxygen being present. The gas was then mixed with several volumes of pure electrolytic hydrogen, and run into a eudiometer over mercury with a little conc. sulfuric acid on its surface. Continuous sparking across platinum electrodes within the tube produced a continuous reduction of volume and the deposition of a white solid on the acid-wet portion of the inner walls of the tube. In one experiment 0.7610 g. of *bis*-triphenylhydrazine gave 33.38 cc. of gas (0°, 760 mm.). The theoretical value for the evolution of all the nitrogen as N_2 is 33.02 cc. A portion of the gas (20 cc.) was mixed with pure hydrogen (67 cc.) and sparked until the acid threatened to touch the electrodes within the eudiometer. The residual volume was 10.2 cc. or 3.2 cc. over the 7 cc. excess of hydrogen added. The quantity 3.2 cc. is that portion of the original stoichiometric mixture of 80 cc. (20 cc. of N_2 + 60 cc. of H_2) which had not reacted to form ammonia. This amount (3.2 cc.) is 4% of the original 80 cc. Now, the acid solution washed from the eudiometer and analyzed gave 0.0250 g. of ammonia. Twenty cc. of pure nitrogen, measured under the same

[19] Stieglitz and Senior, Ref. 2, p. 2732.

conditions as prevailed for the 20 cc. of gas which was mixed with hydrogen and sparked, would give 0.0261 g. of ammonia. The ammonia found (0.0250 g.) is thus 4.2% less than the theory demands, (0.0261 g.). Since the gas unconverted to ammonia is 4% of the original amount taken and the ammonia found is 4.2% less than theory demands for this same original amount of nitrogen and no other gases were found, the conclusion is drawn that the gas from the thermal decomposition of the hydrazine was all nitrogen.

The solid product of the decomposition of *bis*-triphenylmethylhydrazine appeared in part as a snow-white sublimate and in part as a residual solid in the bottom of the test-tube. Samples of sublimate were needle-like crystals and melted at 92°. When mixed with pure triphenylmethane[19] melting at 92° they melted at 92°. The identity of the sublimate is thus established. The remainder of the residual solid was crystallized from benzene and fused to free the crystals from the molecule of benzene present as benzene of crystallization. The product then melted at 92° and mixed with triphenylmethane melting at 92° gave a melting point of 91–92°. A sample of 0.7610 g. of *bis*-triphenylmethylhydrazine decomposed under the conditions previously stated, *i. e.*, in an atmosphere of carbon dioxide by heat in a bath at 220° to 230°, gave 0.6968 g. of residue in the test-tube and 0.0191 g. of sublimate which total 0.7159 g. The reaction equation calls for 0.7197 g. of triphenylmethane. Repeated tests for aniline and aniline derivatives in these residual solids were without exception negative.

These results indicate that *bis*-triphenylmethylhydrazine at its melting point decomposes practically quantitatively into nitrogen and triphenylmethane.

III. A Series of Attempts to Secure Rearrangement of *sym.-bis*-Triphenylmethylhydrazine below its Melting Point or in Solution

In view of this decomposition at the melting point, an effort was made to secure rearrangement in solution or at temperatures below that at which the compound melted. Although the results were negative, the brief description of several may possibly save future repetition.

One-half g. of *bis*-triphenylmethylhydrazine was triturated with 8 g. of anhydrous zinc chloride and allowed to stand protected from moisture for 2 months at ordinary temperature. The mixture darkened during this time, but no trace of aniline could be detected when the mass was worked up and tested according to the method of Stieglitz and Senior.[19] Analogous samples which had stood for shorter lengths of time gave the same negative results.

One-half g. of *bis*-triphenylmethylhydrazine and 8 cc. of dry benzene were heated in a sealed tube at 250° for 30 minutes. The contents of the tube after cooling were found to be under marked pressure. The dark colored solution showed no traces of aniline derivatives but contained nearly pure triphenylmethane. The pressure in the

tube was then due to nitrogen, the same thermal decomposition having taken place as occurs when the solid compound is heated.

A sample of the hydrazine was heated with finely ground dry zinc chloride for 8 hours at 100°. During this time the yellow mixture went through a continuous color change and caked considerably. Although no gas evolution was visible, the residual hydrocarbons melted well below 100° indicating formation of triphenylmethane. No aniline could be found when the test previously referred to was applied.

The *bis*-triphenylmethylhydrazine with ground zinc chloride was heated at 170–180° for 3 hours. Slight evolution of gas could be detected and the mass softened. As before, no aniline could be detected. Triphenylmethane was identified as a product. This indicates that the thermal decomposition of the hydrazine can be secured at temperatures below its melting point by continued heating.

A mixture of *bis*-triphenylmethylhydrazine and zinc chloride was placed in dry benzene and boiled for 7 hours under a reflux condenser at the boiling point of benzene. The condenser had been thoroughly dried and was protected by a calcium chloride tube. Part of the yellow color of the mixture was taken up by the benzene. No aniline could be detected in the resulting solution or products. Triphenylcarbinol was identified as a product. It melted at 158–159°. Mixed with pure carbinol (m. p. 159–160°) it melted at 158–159°.

Bis-triphenylmethylhydrazine (0.065 g.) was mixed with phosphorus pentoxide and heated in a test-tube immersed in an acid bath at 105–110° until no further change in appearance was noticeable (about 2 hours). No aniline or aniline derivatives could be detected in the residue. A portion of the original compound was recovered unchanged.

A sample (0.062 g.) of the hydrazine was put into water (50 cc.) along with a trace of specially prepared platinum black,[20] and held at 50° for 30 hours. The mixture was acidified, heated, made alkaline and distilled with steam. No aniline could be detected in the distillate. The *bis*-triphenylmethylhydrazine was recovered unchanged.

A sample (0.09 g.) of the hydrazine, approximately 0.04 g. of the platinum black and water (20 cc.) were heated in a sealed tube at 170° for 1 hour. Tested as above, no aniline could be detected in the contents of the tube. The original compound was recovered unchanged.

Some of the hydrazine (0.5 g.) was heated with anhydrous aluminum chloride (5 g.) at 180° for 10 minutes. The hydrolyzed products gave no test for aniline. The products were not investigated further.

IV. A Series of Experiments to Determine Conditions for a Maximum Rearrangement by Zinc Chloride

Realizing that a continuance of the experiments to effect the rearrangement at temperatures below that of the melting point of the compound might result only in a vain search for a catalyzer, we decided to return to the original method of Stieglitz and Senior and to secure a greater degree of rearrangement, by a rigorous study of all the conditions involved, than had been obtained in this earlier work.

Accordingly, experiments were carried out under varying conditions and the degree of rearrangement was determined in each case by titration of the aniline recovered with 0.1 N sodium bromate solution.[21] In

[20] Loew, *Ber.*, **23**, 289 (1891). Also see Tanatar, *Z. physik. chem.*, **40**, 475 (1902) and **41**, 37 (1902).

[21] Curme, *J. Am. Chem. Soc.*, **35**, 1162 (1913).

particular the temperature and the time of heating and especially, also, the shape of the vessel in which the reaction was carried out and the time required to heat the mixtures up to the reaction temperature were varied. The results are given in the table that follows. The significance of the first 8 columns is obvious. In the last column is given the result of heating phenylimido-benzophenone under the corresponding conditions with zinc chloride. The first 2 experiments (Nos. 12 and 17) were carried out in hard glass tubes, the next 4 in an Erlenmeyer flask of 60 cc. capacity on the floor of which the mixture was spread in a thin layer and in the last 4 experiments, for the securing of still more rapid heating, a 100cc. Erlenmeyer flask was used. A metal bath was employed and the temperature of the bath taken with the aid of a thermocouple. Since phenylimido-benzophenone, $(C_6H_5)_2C=NC_6H_5$, is probably the actual product formed by the rearrangement and the aniline is obtained by subsequent hydrolysis, parallel experiments under the same conditions were made with this product in order to determine whether it is destroyed by zinc chloride under the conditions of the experiment.

TABLE I

DEGREE OF REARRANGEMENT BY ZINC CHLORIDE

Expt.	Sample G.	ZnCl₃ G.	Temp. °C.	Time Min.	Aniline Found G.	Calc.[a] G.	Aniline recovered from $(C_6H_5)_2C=N-C_6H_5$	
							%[a]	%
12	0.50	5	300	10	0.005	0.09	6	78.5
17	0.50	5	330	5	0.015	0.09	17	90.4
19	0.61	6	330	3	0.024	0.11	22	..
21	0.59	6+	360	3	0.032	0.11	30	..
22	0.51	6+	400	3	0.030	0.09	33	..
23	0.52	7	390+	2	0.033	0.09	37	91.3
24	0.55	7	390+	4	0.031	0.10	31	
25	0.51	7	390+	2	0.028	0.09	31	approxi-
28	0.78	7	450	1³/₄	0.038	0.14	27	mately
29	0.57	7	450	2	0.029	0.10	29	90
30	0.57	7	450	1¹/₆	0.035	0.10	35	
32	0.52	7	450	1¹/₆	0.031	0.09	34	

[a] These values are calculated on the basis of the assumption (Scheme I, p. 4 of the introduction) that each molecule of hydrazine yields one molecule of aniline and not two molecules (as demanded by Scheme II).

The method used in Expts. 30 and 32 was chosen as the best under the working conditions employed. Expt. 23 gave a better yield, but 60cc. flasks of the variety which after careful annealing would stand being plunged repeatedly into a metal bath at the temperatures used were not then immediately available.

The method employed in Expts. 30 and 32 was essentially this. The dry *bis*-triphenylmethylhydrazine was weighed into the specially dried

flask, the anhydrous zinc chloride finely ground in a hot dry mortar added to it and the two were thoroughly mixed. If the *bis*-triphenyl-methylhydrazine is pure and both substances are thoroughly dry, little, if any yellow color appears when the two are mixed. The flask was fitted with an empty 30cm. calcium chloride tube and that closed with a short filled calcium chloride tube. The flask whose contents, protected from the moisture of the atmosphere, had thus been thoroughly mixed and shaken down into a thin layer over the bottom of the flask, was plunged into the molten metal bath at 450°. After 70 seconds it was removed and allowed to cool. The method for working up the product is essentially that described below (p. 18) for the quantitative examination.

Examination and Identification of the Products of Rearrangement

Aniline.—The identity of this compound was established by Senior[19] by the analysis of its chloroplatinate. Besides the observation of the characteristic purple color developed on the addition of calcium hypochlorite solution to the first drops of the steam distillate, the tribromo-aniline obtained from the titration of several of the acidified steam distillates containing aniline, was washed with water, and recrystallized from alcohol. This product melted at 118–119°. When mixed with tribromo-aniline, melting at 119–120°, it melted at 118–120°.

Phenol.—The quantitative preparation of phenol as tribromo-phenol is described below (p. 19). The white precipitates from several titrations[22] were collected on a filter, washed with water and recrystallized from dilute alcohol. The fine, long, white needle crystals melted at 90°. Mixed with tribromo-phenol, melting at 94°, the product melted at 90–92°. The identity of phenol as a product of the reaction is thus established.

Benzophenone.—The quantitative separation of benzophenone in the form of its oxime is described below (p. 19). Our qualitative work by similar methods yielded a considerable quantity of almost pure white crystals of benzophenone-oxime which, when dry, melted at 137–138°. Mixed with benzophenone-oxime melting at 141°, the substance melted at 138–139°. This established the presence of benzophenone among the hydrolyzed rearrangement products.

Diphenylene-phenylmethane and Triphenylmethane.—The hydrocarbons obtained (see below, p. 20) melted at 82–83°. The melting point of this material[19] was not raised by further recrystallization from alcohol or benzene. However, in concentrated ether solution by a careful regulation of the rate of the spontaneous evaporation of the solvent, two distinct types of crystals were formed. One consisted of groups of fine needles growing from a common center; the other was made up of a relatively small number of large bar-like crystals. Both were colorless

[22] See Koppeschaar, *Z. anal. Chem.*, **25**, 162 (1886).

and the two were mechanically separated with ease. The first melted at 143–144° without purification. Recrystallization from alcohol gave it a constant melting point of 145–146°. Diphenylene-phenylmethane, prepared according to Kliegl[23] and freed from triphenylmethane, formed at the same time, and by repeated crystallization from alcohol, melted at 145–146°. An equal part mixture of the two compounds of this melting point melted at 145–146°. This established the identity of the diphenyl-ene-phenylmethane produced in our reaction.

The larger crystals after being pressed between two filter papers melted at 92° without further purification. Mixed with triphenylmethane melting at 92°, they melted at 92° and hence were triphenylmethane.

Triphenylmethane and Gum Resin.—From the resins left by steam distillation, only triphenylmethane (m. p. 91°, identified as usual) was isolated.

V. The Decomposition of Triphenyl-methylamine at 450° in the Presence of Zinc Chloride and the Establishment of the Existence of Triphenyl-methylamine as an Intermediate Product in the Rearrangement of *sym.-bis*-Triphenylmethylhydrazine

Despite the thorough search made for triphenyl-methylamine and its hydrolytic product, triphenylcarbinol, among the rearrangement products, neither could be found. The properties of triphenyl-methylamine are such that quantities of it along with some triphenylcarbinol should have been found without difficulty, principally in the gummy residue of the steam distillation made in the determination of the aniline, if it were present in the melt resulting from the heating of *bis*-triphenylmethyl-hydrazine with zinc chloride to effect the rearrangement. Since none was found and its formation in the rearrangement was suggested by the theory under investigation, its decomposition by zinc chloride after its formation was indicated. Hence, it became essential to know the effect of heating triphenyl-methylamine with zinc chloride under conditions identical with those used to produce rearrangement of *bis*-triphenylmethylhydrazine. Accordingly, triphenyl-methylamine was prepared from triphenylmethyl bromide and dry ammonia.[24] To insure its being free from the hydro-bromide, it was extracted in a Soxhlet apparatus with low-boiling ligroin.[25] It melted at 103° after crystallization from the ligroin. The following experiments were then carried out.

Triphenyl-methylamine (1.5 g.) was mixed with finely ground anhydrous zinc chloride (8 g.) and heated at 450° for 70 seconds, exactly as described in the previous section for the rearrangement of the *bis*-triphenylmethylhydrazine. The melt was treated with

[23] Kliegl, *Ber.*, **38**, 287 (1905).

[24] Elbs, *ibid.*, **16**, 1276 (1883).

[25] This method of purification of triphenyl-methylamine is due to Mr. H. C. Trimble of this Laboratory, whose dissertation is, as yet, unpublished.

ordinary ether and the resulting dark red solution was filtered from a dirty-white insoluble solid portion (A).

The solution was shaken with conc. sodium hydroxide solution, the ether portion separated, dried with anhydrous potassium carbonate and solid sodium hydroxide, and evaporated to dryness. The residue was dried *in vacuo* over solid potassium hydroxide. It was taken up in absolute ether and, because the solution was not quite complete, the ether extract was filtered. Dry hydrogen chloride, passed into the solution, gave a flocculent precipitate (B). The solution after filtration was partially decolorized with charcoal and evaporated to dryness. The residual gum was freed from ether *in vacuo* and dissolved in a little benzene. Crystallization took place rapidly. A portion of the crystals pressed between filter paper, fused on the steam-bath and allowed to solidify, melted at 90–91°. A mixture of this with triphenylmethane in equivalent quantities melted at 91–92°.

The insoluble material[26] (A) when covered with a little conc. sodium hydroxide solution and warmed gave copious quantities of ammonia. It evidently consisted of a zinc ammonium chloride.

The precipitate (B) was a clay colored, slimy material, which caked on the filter paper as it dried. It was very slightly soluble in alcohol and insoluble in water, in ether and in ligroin. It dissolved in chloroform and benzene, but crystallized from neither. On evaporation of these solvents both spontaneously and by heat no crystals could be obtained and the residue was a resin. When precipitated from either of these solvents by the addition of low-boiling ligroin, the substance was a clay colored, amorphous material. Examination under the microscope showed no crystalline material. It gave no test for chlorine or the chloride ion. Repeated treatment with conc. ammonium hydroxide produced no change in its properties. It possessed no melting point but darkened and shrank into a hard resin above 220°. Even at 290° no fusion had taken place. This cannot be the hydrochloride of unchanged triphenyl-methylamine.

In a further experiment the melts from two more samples of the fusion of triphenylmethylamine with zinc chloride were washed into separate flasks, treated with alkali and distilled for ammonia in the usual way.

Analyses. Subs., (1) 0.5805, (2) 0.5402. Calc. for triphenyl-methylamine: NH_3, 0.0381,[27] 0.0355. Found: 0.0366, 0.0345.

The melt from a third sample was dissolved in ether and dil. hydrochloric acid. Each of the two solutions, after being well shaken and separated, was washed thoroughly with the other solvent. The portions of like solvents were combined. The aqueous portion containing the zinc chloride and the ammonia was rendered strongly alkaline and distilled for ammonia.

Analysis. Subs., (3) 0.5916. Calc.: NH_3, 0.0388. Found: 0.0384.

This result, in view of the separation of the ether and aqueous portions before distillation and the fact that no triphenylcarbinol was obtained from the distillation residue in (1) and (2), eliminates the possibility of any hydrolysis of unchanged triphenylmethylamine in the first two determinations. Hence, we conclude that triphenylmethylamine, when heated under the conditions previously stated, gives up its nitrogen as ammonia practically quantitatively.

In the distillate of Determinations 1 and 2 were small quantities of solid hydrocarbons which, on crystallization from the ether with which they were extracted, melted at 143–144°. Recrystallized from alcohol and mixed with diphenylene-phenylmethane

---

[26] The exact nature of this zinc chloride ammonia complex was not investigated.

[27] This value was calculated on the basis of one molecule of NH_3 for one molecule of triphenyl-methylamine.

melting at 145°, it gave a melting point of 142–143°. Diphenylene-phenylmethane is thus identified as one of the products of decomposition.

As in the other experiment the residue from the ammonia Distillations 1 and 2 and the ether solution of 3 yielded triphenylmethane and gum or resin.

A sample of triphenyl-methylamine heated alone at 450°, as before, gave a strong odor of ammonia and a residue of triphenylmethane, diphenylene-phenylmethane and resin. This decomposition is entirely analogous to the thermal decomposition of triphenylmethyl bromide and triphenylmethyl chloride in which, respectively, hydrogen bromide and hydrogen chloride together with triphenylmethane, diphenylene-phenylmethane and resin are obtained;[28] and the decomposition with zinc chloride present is not unlike the decomposition of triphenylcarbinol when heated with solid phosphoric acid,[23] except that, in the latter case, water is removed instead of ammonia, the quantity of diphenylene-phenylmethane formed is much greater and the quantity of resin is very small.

In a further experiment a sample of triphenyl-methylamine (0.294 g.) with zinc chloride (8 g.) was heated as before at 450° for 70 seconds. The melt was dissolved in ether and hydrochloric acid, and the ether portion was separated and shaken with 20 cc. of 2 N sodium hydroxide solution. The alkali extract was rendered acid and distilled with steam. The first portion (1 cc.) was divided into three parts and tested for phenol as follows: (1) by the addition of ferric chloride; (2) by the addition of Millon's reagent and then nitric acid;[29] (3) by boiling with dil. nitric acid which will reveal traces of phenol by the odor of o-nitrol-phenol in the hot solution. All tests failed to detect any phenol. A parallel experiment with phenylimido-benzophenone (0.220 g.) yielded negative results in all three tests.

All the decomposition products of triphenyl-methylamine had been recovered from the melt of bis-triphenylmethylhydrazine and identified as such except ammonia. Bis-triphenylmethylhydrazine (0.901 g.) and finely ground dry zinc chloride (10 to 11 g.) were therefore heated under the conditions and in the manner previously described for this compound. The melt was treated with ether and a small quantity of water. The aqueous portion when made strongly alkaline with concentrated sodium hydroxide and warmed, gave a strong odor of ammonia. The gaseous ammonia turned moistened red litmus paper blue and gave a heavy brown precipitate with Nessler's reagent.

Another sample of bis-triphenylmethylhydrazine (0.5 g.), without being mixed with zinc chloride, heated at 450° gave no detectable ammonia, neither was any aniline to be detected in the hydrolyzed products; while a sample (0.2295 g.) of phenylimido-benzophenone[30] heated in the same way gave 83% of the theoretical amount of aniline. The ether solution of the hydrocarbons from this heating of bis-triphenylmethylhydrazine, after decolorization with a little charcoal, yielded only triphenylmethane on complete evaporation. This melted at 90–91°. Apparently bis-triphenylmethylhydrazine does not rearrange when it is heated in the absence of zinc chloride, and ammonia is not produced when the rearrangement does not take place.

[28] Elbs, *Ber.*, **17**, 701 (1884). Hemilian, *ibid.*, **7**, 1208 (1874); *ibid.*, **11**, 837 (1878). E. and O. Fischer *ibid.*, **11**, 613 (1878); *Ann.*, **194**, 257 (1878). Nef., *ibid.*, **309**, 167 (1899). Schwarz, *Ber.*, **14**, 1522 (1881).

[29] Almen, *Jahresber.*, **1878**, 1079.

[30] This product was prepared by the reaction of Reddelieu, *Ber.*, **42**, 4760 (1909), but purified as follows. At the end of the reaction, the melt was shaken with strong alkali, separated and distilled *in vacuo* to remove the excess of aniline. The well-cooled residue was freed from the remainder of the aniline on a cold porous plate and twice recrystallized from dil. alcohol. The product formed beautiful yellow flaky crystals, analyzing on hydrolysis for the calculated amount of aniline.

There can be little question but that triphenyl-methylamine was a primary product of the rearrangement and subsequently underwent the characteristic decomposition of that compound as outlined in the preceding paragraphs. This is established by the following facts holding for the conditions of the rearrangement of *bis*-triphenylmethylhydrazine: (1) triphenyl-methylamine gave practically a quantitative yield of ammonia; (2) benzophenone-phenylimide does not yield ammonia; (3) triphenyl-methylamine gave no hydrocarbon products not found among those of *bis*-triphenylmethylhydrazine; (4) *bis*-triphenylmethylhydrazine did not give ammonia when it did not undergo rearrangement and did give it when it did rearrange; (5) the molecular nitrogen and the triphenylmethane from the portion that underwent thermal decomposition and the phenol present could not give ammonia. Further evidence bearing out this conclusion is to be found in the quantitative study of the rearrangement products.

VI. The Quantitative Study of the Rearrangement Products of *sym.*-*bis*-Triphenylmethylhydrazine

For a quantitative study of this rearrangement, approximately 15 g. of *bis*-triphenylmethylhydrazine was worked up in small portions. For the best yield of aniline under the conditions employed portions of about half a gram should have been used. Individual yields in this series (Table II) were sacrificed somewhat for total quantity of material worked up. Expts. 39 to 47 represent single samples, while in Expts. 47 to 51 two samples were heated separately and then combined for analysis in each experiment. The ratio of the hydrazine to zinc chloride was about 1:10. The preparation and heating of samples were as given in detail in the previous series of rearrangements.

After cooling the melt, it was treated with ordinary ether and a little dil. hydrochloric acid which took most of it into solution. The mixture was heated for several minutes under a reflux condenser to hydrolyze the phenylimido-benzophenone;[31] it was shaken thoroughly and, finally, the two solutions were separated carefully. The aqueous portion was extracted thrice with ether. Each of these ether extracts was washed with dil. acid. The original ether solution was washed twice with dil. acid. The acid portions were combined and likewise the ether portions and the combined portions filtered. This gave three products, (a) the acid portion, (b) the ether portion, and (c) the insoluble portion.

The acid portion (a) containing the ammonia, zinc chloride and the aniline formed by the hydrolyzed phenylimido-benzophenone was made strongly alkaline in a closed apparatus and distilled with steam into 20 cc. of 6 N sulfuric acid. The distillate (400 cc.) was extracted with alcohol-free ether to remove any hydrocarbons,[32] freed from any

[31] The completeness of this hydrolysis was tested in this way: 0.2297 g. of phenyl-imido-benzophenone was treated as indicated in the text and the aqueous portion titrated for aniline. Calc. for aniline: 0.0831 g. Found: 0.0828 g.

[32] Despite the complete hydrolysis of the phenylimido-benzophenone and the thor-

dissolved ether and titrated for aniline with standard bromate solution. A slight excess of sodium thiosulfate was added and the tribromo-aniline removed by filtration. The filtrate was then made alkaline and the ammonia distilled in the usual manner. Cochineal was used as the indicator.[33]

The ethereal portion (b), containing the phenol, all the hydrocarbons and benzophenone, was shaken with sodium hydroxide solution (15 to 20 cc. of 2 N) and two like portions of water. The combined aqueous portions containing all the phenol[34] were rid of dissolved ether, made acid with hydrochloric acid and distilled with steam into dil. sodium hydroxide (5 cc.). The distillate (300 cc.) was rendered strongly acid and titrated with standard bromate solution for phenol.

The ethereal solution of hydrocarbons and benzophenone from the whole series or rearrangements was distilled nearly to dryness and distilled with steam until the distillate had entirely ceased to be milky in appearance. Solid hydrocarbons were still coming over but the benzophenone was practically all distilled.[35]

The recovery of benzophenone from the hydrocarbon mixture, extracted from the steam distillate, was carried out essentially as described earlier in this paper. The mother-liquor, after the removal of the benzophenone-oxime, was extracted and this extract, together with the mixture of hydrocarbons previously removed, was treated a second time for benzophenone. A very small second crop of the oxime was obtained.

The mixture of triphenylmethane and diphenylene-phenylmethane precipitated from the alkaline solution of benzophenone-oxime, after being washed free from alkali, melted at 80–84°. This was dissolved in a little ether and by a careful control of the concentration, two crops (1.10 g.) of triphenylmethane, m. p. 90°, were removed. The diphenylene-phenylmethane (0.05 g.) was then crystallized, and recrystallized from alcohol. It melted at 145–146°.

The residue from the distillation with steam was extracted with ether and the extract treated with animal charcoal, filtered, dried with calcium chloride, distilled to dryness and freed from ether *in vacuo*. Benzene was added to this residual gum and

ough extraction of the acid portion (a) with ether, there was some neutral product distilled at this point. This proved to be benzophenone melting at 45°. It was added to the ethereal portion (b). This suggests the probability of formation of a complex oxonium salt of benzophenone. The quantity of this material varied greatly. The controlling factors were not investigated but will be determined in this Laboratory. See Maass and McIntosh, *J. Am. Chem. Soc.* **33,** 71 (1911).

[33] The presence of the ammonium salt in no way affected the aniline titration. (See Kingscott and Knight, "Quantitative Organic Analyses," Longmans, Green and Co., **1914,** p. 257; Sutton, "Volumetric Analyses," Blakiston's Son and Co., **1911,** p. 387). The accuracy of the ammonia determination from the filtrate was sufficient for the purpose for which it was used. Some blank experiments gave these results: 0.0345 g. of aniline and 0.1164 g. of ammonium sulfate (NH_3 content, 0.0300 g.) gave 0.0344 g. of aniline and 0.0303 g. of NH_3; 0.0345 g. of aniline and 0.1164 g. of ammonium sulfate gave 0.0344 g. of aniline and 0.0301 g. of NH_3.

[34] The completeness of the separation, and the absence of condensation, of the aniline and the phenol on being heated with a concentrated solution of zinc chloride and hydrogen chloride were tested. A typical experiment gave these results: 0.0345 g. of aniline, 0.0305 g. of phenol and 0.0887 g. of ammonium sulfate (NH_3 content 0.0229 g.) gave 0.0346 g. of aniline, 0.0304 g. of phenol and 0.0232 g. of ammonia.

[35] Benzophenone (0.70 g.) was distilled with steam, the condenser terminating in an adapter which dipped beneath the surface of the distillate as in the aniline, ammonia and phenol distillations. From the first 400 cc. of the distillate 0.672 g. of benzophenone was recovered by extraction.

from it two crops of triphenylmethane crystals, totaling 3.3 g., were obtained. The gum after removal of the crystals was again subjected to distillation with steam until 800 cc. of distillate had accumulated. This distillate on extraction yielded 0.2 g. of hydrocarbons, which were very largely diphenylene-phenylmethane (m. p. 144°). The small amount of contaminating material proved to be triphenylmethane. The residue from distillation with steam (α) was again extracted, dried *in vacuo* and treated with benzene in an effort to obtain further crystallization. The crystals formed were extremely small in amount and were not recovered.

The insoluble residue (c) left after treatment of the melt with ether and aqueous acid, was subjected, in the original filter papers, to extraction in a modified Soxhlet apparatus with chloroform as the solvent. This gave a carbonized residue (β) and a chloroform solution of a resin-like material (γ) in no way distinguishable from the precipitate (B) described in connection with the decomposition of triphenyl-methylamine, except that it was darker in color. This will be discussed later.

A portion (1.12 g.) of the benzophenone-oxime recovered was dissolved in alcohol, dil. hydrochloric acid added and the solution boiled for several hours; it was then diluted and extracted with ether. The dried extract yielded an oil which crystallized on being seeded with a crystal of benzophenone. This weighed 1.02 g. and melted at 45°. Recrystallized from ligroin it melted at 47.5° to 48°.

The identification of each of the compounds obtained was carried through again as follows.

MELTING POINTS

Compound	Found °C.	Known compound °C.	Mixed sample °C.
Ammonia	....	....	....
Tribromo-aniline	118–119	119–120	118–120
Tribromophenol	91–92	92–93	92–93
Benzophenone			
as oxime	139.5	141	140–141
as benzophenone	47.5–48	48	47
Triphenylmethane			
(from the steam distillate)	90	92	90–91
(from the steam distillation			
residue)	90–91	92	90–91
Diphenylene-phenylmethane	145–146	145–146	145–146

The gum or resin (α) residue from the distillation with steam and removal of triphenylmethane was apparently identical with that obtained in the decomposition of triphenyl-methylamine and as such was considered as a final product.

The residue (β) from the chloroform extraction of insoluble portion (c) from the original melt was in no way distinguishable from carbon in its behavior in a flame and its total insolubility in benzene, a characteristic of free carbon.

As previously stated the residue (γ) after evaporation of the chloroform was identical in every way but depth of color with the material obtained from the decomposition of triphenyl-methylamine. It showed the same solubilities and when precipitated from chloroform with low-boiling ligroin and dried, it gave the caked smear. Repeated precipitation failed to purify or change it. When heated in a melting-point tube, it darkened and shrank from 225–230° up (heated to 290°) but never melted so as to spread on or stick to the tube. After the heating, the material was shaken out of the tube and formed a hard, dark resin. It was probably a highly condensed or polymerized mass. A sample of the precipitated material finely ground was treated in aqueous suspension

with concentrated ammonium hydroxide.   It underwent no change in appearance or the properties evidenced under heat and solvent.   Treatment with other alkalies and acids did not affect it.   These properties are not unlike those exhibited by the very highly polymerized products of the indene and cumarone series and other partly unsaturated bodies.

The quantitative determinations of the rearrangement products of this series are given in the table that follows.   In this table, Part 1 gives the results for aniline, phenol and ammonia: Col. 1 gives the number of the experiment, Col. 2 the weight of samples used (given in values rounded to centigrams but calculated to milligrams), Col. 3 the aniline found, Col. 4 the yield of aniline expressed in percentages of the maximum calculated yield.   In Col. 5 the weight of phenol is given and in Col. 6 the equivalent percentage of aniline, calculated on the assumption that each molecule of phenol represents a molecule of aniline lost in the rearrangement (see the introduction).   In Col. 7 we have the sum of the aniline actually found and of the aniline equivalent of the phenol found.   In Col. 8 the amount of ammonia found is given and in Col. 9 the percentage of the calculated yield found, figured on the basis of the assumption that each molecule of hydrazine gives by way of triphenyl-methylamine a molecule of ammonia.   In Part 2, the results for benzophenone are summarized, the calculations being based on the 23.94% of rearranged substance shown by the aniline of the total of Col. 4 of the first part of the table.   In Part 3 the yields of other products are given in grams.

TABLE II

QUANTITATIVE DETERMINATION OF THE REARRANGEMENT PRODUCTS

1. Aniline, Ammonia and Phenol

1	2	3	4	5	6	7	8	9
		Aniline found		Phenol found	An. eq.	Sum of aniline and an. eq.	Ammonia found	
No.	Sample	G.	% of Calc.	G.	%	%	G.	%
39	0.77	0.040	28.8	0.035	25.1	53.9	0.016	64.0
40	0.77	0.043	31.0	0.030	21.6	52.6	0.014	56.0
41	0.65	0.026	22.2	0.032	27.4	49.6	0.013	61.9
42	0.76	0.028	20.4	0.038	27.8	48.2	0.016	64.0
43	1.02	0.046	25.0	0.037	20.5	45.5	0.021	61.8
44	1.35	0.053	21.8	0.067	27.3	49.1	0.031	69.0
45	1.54	0.038	13.7	0.048	17.3	31.0	0.026	51.0
46	0.52	0.027	28.7	0.029	30.9	59.7	0.0115	67.6
47	1.61	0.071	24.5	0.067	22.7	47.2	0.0321	60.4
48	1.46	0.069	26.2	0.074	28.2	54.4	0.033	68.7
49	1.61	0.072	24.8	0.074	25.2	50.0	0.031	58.5
50	1.50	0.068	25.2	0.075	27.4	52.6	0.033	67.3
51	1.55	0.071	25.5	0.080	28.3	53.8	0.033	64.7
Total	15.11	0.652	23.94	0.686	24.94	48.9	0.3105	62.3

2. Benzophenone

Sample taken	Benzophenone-oxime		Benzophenone	
	Found	Calc.	Found	Calc.
15.12	1.22[36]	1.38	1.12	1.27

3. Other Products

	From steam distillate G.	From steam distillate residue G.	Total G.
Triphenylmethane..............	1.10	3.30	4.40
Diphenylene-phenylmethane......	.25	..	0.25
Gum resin-steam dist. residue.....	..	6.35	6.35
Carbonized residue (β)...........	..	..	0.30
Resinous material (γ)............	..	..	0.35

VII. Rearrangements of *sym.-bis*-Triphenylmethylhydrazine in Other Atmospheres than Air[37]

With a view to the study of the rearrangement and the coincidental thermal decomposition by accounting for the whole of the nitrogen of the molecule in the products found, attempts were made to secure the rearrangement of the hydrazine in an atmosphere of carbon dioxide. It was expected that possibly a relation could be found between the percentage of the *bis*-triphenylmethylhydrazine that underwent the primary decomposition into nitrogen and triphenylmethane and the percentage of the *bis*-triphenylmethylhydrazine which underwent the rearrangement, and that by the measurement of the nitrogen evolved and the aniline produced at various temperatures, the extent of the thermal decomposition and of the rearrangement would be given. It was proposed to begin at temperatures below 300°, this being the only temperature at which, at that time, the arrangement had been effected.[38] Accordingly, the following experiments were carried out.

A sample (0.514 g.) of *bis*-triphenylmethylhydrazine was weighed into a hard glass tube, 5 g. of finely ground anhydrous zinc chloride added and the two intimately mixed. The tube was connected with a source of dry carbon dioxide and by an outlet to a nitrometer. When the apparatus had been freed from air, the tube was immersed in an oil-bath at 275° and retained there until nitrogen had ceased to be evolved. The nitrogen collected amounted to 3.7 cc. at 23° and 738.1 mm., uncorrected. The melt was dissolved out with ether and water, washed well with conc. sodium hydroxide solution,

[36] One g. of benzophenone and 2.3 g. of triphenylmethane yielded 0.95 g. of benzophenone-oxime and 2.27 g. of triphenylmethane when the mixture was treated as outlined in the text of this paper. Calc., 1.08 g. of the oxime. Hence 1.22 + 0.13 = 1.35 g. of the oxime calculated (1.38) in the text is accounted for.

[37] This work was done before the decomposition of triphenyl-methylamine was investigated and the presence of ammonia among there arrangement-decomposition products of *bis*-triphenylmethylhydrazine was discovered and its quantity taken as the measure of the minimum portion of the *bis*-triphenylmethylhydrazine which originally split into triphenyl-methylamine and the univalent nitrogen derivative, which rearranges to give phenylimido-benzophenone and phenol.

[38] By ourselves and by Stieglitz and Senior, Ref. 19, p. 2731.

hydrolyzed and distilled with steam after the addition of sodium hydroxide. No aniline could be detected in any portion of the distillate with calcium hypochlorite solution. The solid hydrocarbons in the distillate softened from 70° up and melted at 78–84°. Beyond this they were not investigated at this time.

A sample (0.664 g.) of *bis*-triphenylmethylhydrazine was treated as above except that a temperature of 300° was used. The evolution of the nitrogen seemed to be complete in about 3 minutes and it had all been swept over at the end of 10 minutes. The gas collected amounted to 6.8 cc., at 24° and 752.5 mm., uncorrected. As before, all efforts to detect aniline among the hydrolyzed products failed. The hydrocarbons extracted from the distillate with steam melted at 78–81° and, mixed with an equal quantity of triphenylmethane melting at 92°, melted at 85–88°. They were not further investigated.

After the rearrangement in air had been developed to give a yield of 35% of the calculated amount, the conditions of temperature, time, and container and methods of manipulation were applied to secure rearrangement in carbon dioxide. Four experiments were made. A mixture of 0.518 g. of *bis*-triphenylmethylhydrazine and 7 g. of zinc chloride prepared as described earlier in this paper was heated in an atmosphere of carbon dioxide, prepared by the heating of pure sodium hydrogen carbonate, and dried by being passed through 2 sulfuric acid wash-bottles. After the flask had cooled it was immersed in an ice-bath and the nitrogen swept into the nitrometer. The melt was lighter in color than those produced in air, being brown, and had no odor of phenol but one resembling that of *diphenyl*. It was dissolved in ether and water; the resulting solutions were shaken with conc. sodium hydroxide solution and the ethereal solution separated. To this ethereal extract, aqueous and ethereal solutions of hydrogen chloride were added, and the ether was distilled. The residue was warmed for 20 to 30 minutes on the water-bath, made alkaline and distilled with steam. No trace of aniline was found in the distillate. The hypochlorite test as applied easily detected 0.01 mg. of aniline in the same volume of solution.

The above experiment was repeated with 0.556 g. of *bis*-triphenylmethylhydrazine. Fifty cm. of tubing filled with glass beads covered with phosphorus pentoxide had been added to the drying system. The first few drops of the distillate gave a very faint coloration with the hypochlorite solution. The test was considered exceedingly doubtful.

The experiment was again repeated with 0.616 g. of *bis*-triphenylmethylhydrazine, the carbon dioxide being generated from pure magnesite. The first portion (1 cc.) of distillate in this case gave an appreciable color with hypochlorite solution. The color was not quite the characteristic purple but may have been affected by the opalescence of the distillate due to the hydrocarbons present.

One more experiment was made with 0.501 g. of the *bis*-triphenylmethylhydrazine. As in the last experiment, the first portion (1 cc.) of the distillate with steam gave a coloration with the hypochlorite solution.

In each of these experiments the first 400 cc. of the acid distillate with steam was extracted, freed from dissolved ether and titrated with standard bromate solution. Some bromate solution was used up and varied in amounts equivalent to 2 to 5 mg. of aniline. In no case, however, was there a precipitate of tribromo-aniline, while 3 mg. of aniline gives a marked precipitate of tribromo-aniline. Further, after extraction of the distillate in the fifth experiment, it was diluted to exactly 500 cc. and divided into two 250 cc. portions. One portion was rid of dissolved ether and then titrated with standard bromate solution. It required 0.71 cc. of the solution. The second portion (250 cc.) was made alkaline, extracted, acidified and titrated. This portion required 0.72 cc. of the bromate solution. The extract of the second portion, on being evaporated in a very slow stream of dry air, yielded no residue. The distillate of Expt. 4 was extracted 10 times with a total of 500 cc. of ether free from alcohol, and required

approximately the same quantity of bromate solution as the other distillates. After the standard solutions used in these titrations had been checked, and 0.0070 g. of aniline out of the 0.0101 g. theoretically possible had been recovered from 0.0279 g. of phenyl-imido-benzophenone on treatment identical with that applied to the *bis*-triphenylmethyl-hydrazine, it was concluded that if any phenylimido-benzophenone was formed by re-arrangement in any of these experiments, it was exceedingly minute in amount. Traces of aniline, if proved, could be explained by the presence of the 0.4 to 0.5 cc. of air found to be occluded by the zinc chloride and freed when heated as described above.

The hydrocarbon extracted from the distillate with steam on evaporation of the ether proved to be triphenylmethane melting at 88–90°, while the steam distillation residue in benzene solution yielded triphenylmethane crystals which after being washed with ligroin melted at 88–89°.

The nitrogen evolved in these last four experiments varied from 50 to 75% of the total nitrogen in the sample taken.

Although *a priori* reasons make it unlikely that phenol was formed in these ex-periments (see the introduction), the alkaline sodium zincate solutions from the fourth, fifth and sixth experiments were saturated with carbon dioxide and extracted with ether. The extracts were allowed to evaporate spontaneously. The residues showed no test for phenol on the addition of ferric chloride.

These results, in the light of those from the rearrangements in air, raise the rather serious question as to whether the oxygen of the air is productive of the rearrangement or whether the carbon dioxide exerts an inhibitive influence on it. Qualitative and quantitative determinations of the ammonia in the products of the attempted rearrangements in carbon dioxide will show whether the carbon dioxide prevents completely the primary splitting into triphenyl-methylamine and the univalent nitrogen derivative which rearranges to give benzophenone-phenylimide, or only prevents this latter rearrangement after the splitting has occurred. If the splitting does occur, it is much less in carbon dioxide than in air, in view of the amounts of nitrogen and of the hydrocarbon products found. It is considered doubtful that the splitting occurs, but only ex-perimental study which includes data on the amounts of ammonia formed can determine that. With data available on the rearrangement in an atmosphere of nitrogen or *in vacuo* a quantitative study of the ammonia, aniline and phenol as well as the other products from rearrangements effected in mixtures of oxygen and nitrogen, in which the percentage of oxygen is made to vary from zero to that of the air, should shed valuable light on the true part oxygen plays in the rearrangement.

Two arrangements, one in air and one in oxygen, carried out simul-taneously in the same metal bath and with a 100cc. Erlenmeyer flask gave these results.

	Sample G.	ZnCl₂ G.	Temp. °C.	Time heated Sec.	Aniline found G.	Phenol found G.	Aniline calc. G.
Air..........	0.5192	7	450	70	0.0307	0.0279	0.0936
Oxygen......	0.5701	7	450	70	0.0307	0.0318	0.1028

Because of difficulties in securing exactly duplicate physical conditions

conclusions cannot safely be drawn on less than a whole series of such measurements, together with the quantitative determinations of the ammonia produced in each arrangement.

Summary

Our conclusions may be summarized as follows.

1. The formation of an aniline derivative by the rearrangement of *sym.-bis*-triphenylmethylhydrazine, as observed by Senior and the one of us, was fully confirmed.

2. Benzophenone was isolated as a product of the hydrolysis of the presumable primary rearrangement product phenylimido-benzophenone.

3. The decomposition products of triphenyl-methylamine, namely, ammonia and diphenylene-phenylmethane and triphenylmethane, which are formed when triphenyl-methylamine is heated with zinc chloride, were also found in quantity in the reaction products and the conclusion drawn that triphenyl-methylamine is a primary product of the action studied and is then decomposed in the manner indicated.

4. Triphenylmethane and nitrogen were proved to be products of the thermal decomposition of the hydrazine, the result of an intramolecular oxidation-reduction in a direction reverse to that which causes the rearrangement.

5. Phenol was obtained in quantity when the rearrangement reaction was carried out in air but none was found when the action was carried out in an atmosphere of carbon dioxide. The hypothesis has been tentatively formulated that the formation of phenol is due to the capture of oxygen by escaping migrating phenyl radicals.

·6. In support of this view the sum of the aniline and the phenol obtained was found to be roughly equal to the total amount of ammonia formed.

7. The observation was made that there is apparently no rearrangement in the absence of air, a result which demands further investigation of the possibility that the rearrangement is the result of an oxidation reaction in which the oxygen of the air takes part.

8. The interpretation of the reactions from the point of view of the theory of electronic valences is given and accords well with the explanation of other rearrangements of this general type.